10.

[*Extracted from the* Geological Magazine, Vol. X. No. 10. October, 1873.]

ON ANALYSIS OF WHITE CHALK FROM THE COUNTY OF TYRONE, WITH NOTE ON THE OCCURRENCE OF ZINC THEREIN, AND IN THE OVERLYING BASALT.[1]

By Edward T. Hardman, F.R.G.S.I.; of the Geological Survey of Ireland; Associate of the Royal College of Science, Dublin.

I WAS led to make this analysis with the view of determining if possible whether the extreme hardness of the Irish Chalk were due to either a chemical, a mechanical, or a calorific alteration, from the influence of the overlying basalt. If it were owing to chemical change, we should expect to find a large per-centage of silicates and a diminution in the amount of lime; if to the influence of heat, carbonic acid would be driven off, silica would be in excess, and the presence of the insoluble bases, such as the peroxide of iron, oxide of manganese, and alumina, would become more apparent; while if a mechanical cause or pressure were the reason, no change would take place in the relative amount of the constituents. I believe the result seems to show that the induration of the Chalk must be set down chiefly to the last agency,—if to anything apart from the original formation of the rock,—and that the power of alteration exerted over it by the heat of the molten basalt has been small indeed. At the same time a certain addition has been made to it by means of water holding chemical bodies in solution.

The following is the result of the analysis. The specimens used were obtained from an old quarry in the townland of Legmurn, about a mile and a half north-east of Stewartstown. The Chalk is so indurated as to be in reality a hard splintery limestone.

$CaCO_3$	97·320	ZnO	traces.	Very perceptible even in small quantities of the Chalk.
$MgCO_3$	0·890			
SiO_2	0·537	BaO	a trace.	
Al_2O_3	0·273	SrO	a trace.	
Fe_2O_3	0·095	K_2O	Amount not estimated.	
FeO	a trace.	Na_2O		

By the kind permission of Prof. Galloway the quantitative analysis 99·105 was made in the laboratory of the Royal College of Science, Dublin.

As the potash and soda were very small in quantity, it was not worth while to estimate them, and the residue insoluble in hydrochloric acid, amounting to but 1·565 grains in 297·5 of the limestone, was considered to be silica, being too small to analyze.

There is nothing remarkable about the other constituents, except the presence of zinc, which I believe it is unusual to find disseminated in an invisible form over a large extent of rock, even in trifling local amount. At any rate I have never seen it given in such analyses as I have met with, of limestone or other rock,—although its ores are known to be often associated with the former; but for the most part as subsequent deposits in cavities of erosion.

I happened to discover its presence in the Chalk accidentally, while

[1] Read before the Geological Society of Ireland, June 11, 1873.

examining it in the wet way for titanic acid, which I imagined might be expected to result from the decomposition of titano-ferrite in the overlying basalt. The titanic acid did not reveal itself, but a strong indication of zinc appeared. I then determined to test it in the dry way, and on fusing some of the powdered chalk with carbonate of soda on charcoal, I was able actually to reduce a small portion of the metal so as to obtain a few spangles of it. These, when subjected to the proper tests, gave the usual re-actions with the blow-pipe which characterize zinc compounds. I repeated this experiment several times with different specimens of the Chalk, and was able to satisfy myself fully of the presence of the metal in it.

As from some of these trials zinc appeared to be in such quantities that it might be estimated, 297·5 grains of the powdered chalk were taken, dissolved in hydrochloric acid, treated with sulphuretted hydrogen, in the expectation that some of the metals precipitable by it were present; silica, iron, and alumina were removed, and it was finally examined for zinc. This was unmistakably proved to be present, but unfortunately in too small a quantity to weigh. In fact it appears to be unequally disseminated throughout the rock, for while in some very small portions submitted to qualitative analysis it was extremely perceptible, yet in the large quantity above named it seemed disproportionately small.

It thus became a question whether the metal occurred merely locally, or was widely scattered over a large area of the Chalk. I therefore examined a specimen of hard white chalk from Slieve Gallion Carn, in the Co. Derry, some eight miles, as the crow flies, north-west of Legmurn. It occurs there as an outlier on the New Red Sandstone, and underlies the basalt. The specimens obtained here lay but two feet below the basalt, but could not be distinguished in appearance from the others, which were taken at some distance from the edge of the dolerite. It contained a few slightly reddened flints however. The examination was only made for zinc, and was done as before, by fusing a portion with carbonate of soda before the blow-pipe.[1] As was expected, the metal was here also reduced, and was perfectly visible, apparently in the same quantity as in the first specimen. Its presence was then confirmed by other tests.

Although this of course affords no direct evidence as to the existence of the metal throughout the chalk here, it is curious that it should be detected in samples procured at such a distance from each other if it were not so.

The idea then arose that it might have been carried down from the basalt in aqueous solution. Accordingly a piece of the basalt which crops out about 160 yards north-east of the Chalk Quarry in Legmurn was procured,[2] and examined in the same way as the Chalk had been. In this also zinc was discovered, and in very appreciable amount; so much so, that I doubt not had I had time to make a quantitative determination, I should have been able to estimate it.

[1] Fletcher's hot-blast gas blow-pipe was used, and by its means a comparatively large quantity of the powdered chalk and of the basalt (see *post*) could be treated.

[2] The spot from which the basalt was obtained is about 300 yards from the Chalk Quarry.

There can be little doubt, therefore, the zinc that occurs in the Chalk, probably as carbonate, which would be indistinguishable on inspection, has been carried down from the basalt in aqueous solution. In what form it exists there however must be uncertain.

[It is true that in most mineralogical works there is no direct mention of the occurrence of zinc compounds in igneous or volcanic rocks,[1] but it seems to be implied in one or two instances; and it certainly appears to be quite possible that many of them would be formed both in the wet and in the igneous way, in such rocks. At first sight it might be surprising that such a volatile metal as zinc would withstand the great heat of molten rock and remain undissipated; yet several zinc minerals have been artificially formed in furnaces, and under other applications of heat. Franklinite, a variety of magnetite containing zinc and manganese, found workable in the metamorphic Silurian limestone of New Jersey, has been imitated by Delesse, by the action of sesquichloride of iron and chloride of zinc on lime, under the influence of heat.[2] Zincite or red oxide of zinc has been obtained in the iron furnaces of Silesia and New Jersey, and in zinc furnaces at Siegen.[3] Blende has resulted artificially from subjecting heated oxide or silicate of zinc to the vapour of sulphur, and is found in the furnaces at the Freiberg smelting works.[4] "It occurs in both crystalline and sedimentary rocks."[5]

[Thus it would seem to be very possible for some zinc compounds to have had a contemporaneous origin with the basalt. On the other hand, the zinc may have been introduced at a later period by the agency of water, in the same way that carbonates of lime, magnesia, and iron, have been, and notably the zeolites, which are so abundant in that rock. This is perhaps the most likely to happen; but in either way, most of the zinc minerals might have been brought in. There is nothing therefore remarkable in the fact of the metal being detected; and it might be met with oftener were it looked for during the analysis of rocks, just as other metals known to exist in certain rocks seldom appear in their published analysis.

[It can only be a matter of surmise as yet with regard to the form in which the zinc exists in the basalt. A possibility might be suggested, however, that some of the magnetite which is found as an accessory mineral in that of Antrim[6] may be of the variety Franklinite. Some of the spinels also, to which this is allied,[7] and which themselves number a zinc compound, have been found in vesicular cavities of the volcanic rocks of Monte Somma;[8] and at least one instance is given of the discovery of *metallic* zinc in basalt. It is

[1] Mr. Thomas Davies, F.G.S., of the Department of Mineralogy in the British Museum, informs me that Professor Scacchi, of Naples, states that Blende (Zn S) occurs occasionally—in association with galena—in the volcanic breccias of Monte Somma.—Edit. Geol. Mag.

[2] Dana's System of Mineralogy (1868), p. 153.

[3] *Ibid.* p. 135.

[4] *Ibid.* p. 50. (Here, too the removal of the obnoxious zinc from the lead is a most difficult problem. See Percy's Metallurgy of Lead, p. 325.)

[5] *Ibid.* p. 49.

[6] Prof. Hull "On the Structure of Trap Rocks," Geol. Mag. April, 1873.

[7] Manual of Geology (Jukes and Geikie), p. 63 (Article by W. K. Sullivan, Ph.D.).

[8] Cotta, Rocks Classified and Described, p. 61.

said, by G. Ulrich, to have been found by a quarryman in a geode in basalt, near Melbourne, Victoria, associated with Smithsonite and cobalt bloom; the specimen weighed $4\frac{1}{2}$ ounces. Dana, however, considers the account to be somewhat doubtful.[1]][2]

With this exception, the analysis shows little that could be ascribed to chemical alteration, nor has there been any loss of carbonic acid, so that the original heat of the superincumbent basalt, which has been so often relied on as the means of hardening the chalk, and reddening the flints, must be quite out of the question. Perhaps a great deal too much power has been ascribed to this agent; as may be conceded when we recollect the unaltered condition of the intervening leaf-beds and lignite, which do not appear to have been affected by it, although naturally very susceptible of its influence.[3]

But when it is remembered that in the Hebrides the basalt reaches a thickness of between 3000 and 4000 feet,[4] and that the Irish basalt, although now but from 500 to 1200 feet thick, may have had similar proportions, there is no difficulty in referring the consolidation of the Irish chalk to pressure alone; for, taking the original thickness of the basalt at only 3000 feet, the pressure on each square yard of underlying chalk would be about 2000 tons.[5]

The analysis, which is extremely similar to one by Mr. Wonfor, of the Chalk of Cushendall, Co. Antrim,[6] shows that it is a limestone of very great purity, the per-centage of siliceous matter being so small as to be quite insignificant. It should therefore be of the highest value in many chemical manufactures, especially that of bleaching powder. But it is remarkable that although in the North of Ireland an immense quantity of this material is used up, it is not made there, but is mostly imported from Glasgow and Lancashire. So far as I know, there is not a single Chloride of Lime Works in Ulster.[7]

[1] System of Mineralogy (1868), p. 17.

[2] The above bracketed portion was added after the paper had been read, as the possibility of zinc occurring in the igneous rocks was disputed at the time. The method of analysis was also said to be unreliable; but it is a far more certain test for small quantities, than the wet process. By it a metal was obtained. This was white and brittle; it dissolved readily in dilute hydrochloric acid; and the solution of the metal heated on charcoal with nitrate of cobalt gave a very distinct bright green incrustation. There is but one metal that exhibits all the above characteristics, and that is zinc.

Voltzite (Zn S+ZnO) occurs at Rosieres, near Pont Gibaud, Puy de Dome (Dana's Mineralogy, p. 50). No mention is made of the rock in which it is found; but in Scrope's "Volcanoes of Central France," both in the maps and in the letter-press (pp. 56, 57), the rocks of that neighbourhood are shown to be granite and recent basalt; no other than igneous rock is laid down on the maps, nearer than about 18,000 metres. (Edition 1858.)

[3] Bischof mentions that small pieces of clay-slate caught up in lava flows were afterwards found to be quite unaltered.

[4] Manual of Geology (Jukes and Geikie), p. 69.

[5] The Chalk of Tyrone is in fact curiously shattered and split up into small irregular parallelopipeds, which appears to be due to more than ordinary jointing. The great pressure may have had something to do with it.

[6] Journ. Royal Dub. Soc., July, 1860.

[7] A quantity of the Antrim Chalk is, however, exported to England for manufacture there.

STEPHEN AUSTIN AND SONS, PRINTERS, HERTFORD.